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THE RELATION OF CHALCEDONY TO THE OTHER FORMS OF SILICA

By Edward W. Washburn and Louis Navias
Department of Ceramic Engineering, University of Illinois

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Silica is known to occur in three distinct enantiotropic forms, each form having two or more enantiotropic sub-forms. These forms are quartz (α and β), tridymite (α, β_1, and β_2) and cristobalite (α and β) to which may be added silica glass, the amorphous or liquid form. The various transition and fusion temperatures and the ranges of stable existence of all of these forms have been accurately determined by Fenner.[1] The position of the mineral chalcedony in this system has, however, never been satisfactorily established, although Fenner seemed inclined to view it as a form different from any of the preceding.

The present investigation is a contribution to the elucidation of the chalcedony puzzle. The method of investigation adopted was a careful determination of a number of physical properties of the raw and calcined chalcedony and a comparison of these properties with those of the four recognized forms of silica. Two minerals belonging to the chalcedony type were used. One of these was a very pure typical chalcedony from Yellowstone Park and the other was a black pebble of French flint.

For comparison a summary of all the data obtained with these materials together with the corresponding data for the four recognized forms of silica is displayed in the accompanying table.

The density data were determined on the finely ground powder by the pycnometer method, the pycnometer and powder being heated to 400° C and evacuated with a mercury vapor pump for several hours before admitting the air-free distilled water. After weighing, a sample of the powder was removed from the pycnometer and while still under water was sent to the Geophysical Laboratory and subjected to a pressure of 1000 atmospheres for two hours. This treatment resulted in a density increase of only six units in the fourth decimal place.

Summary of Results

Results in black face type were obtained in this investigation. After calcination at 1450° for 2 hours the chalcedony analysed 99.87 and the flint 99.6% SiO_2. Inversion temperatures were obtained from cooling curves and volume changes with a dilatometer.

	Raw Chalcedony	Raw Flint	Quartz		Calcined Chalcedony		Calcined Flint		Cristobalite		Tridymite		Silica Glass
			α		α	β	α	β	α	β	α	β	
Specific gravity, 25°/25°	2.55–2.61	2.61–2.63	2.65		**2.175**	...	**2.25**	...	**2.33**	...	**2.27**	....	2.194–2.213
Index of refraction	**1.533–1.538**	**1.533–1.539**	**1.544–1.553**		**1.456–1.470**	...	**1.483**	...	**1.484**	...	**1.475**	....	**1.457–1.460**
Inversion temperature t_I			575°	570°	....	**220°**	...	**227°**	...	**244°**	**117°**	....	None
Coefficient of cubical expansion near t_I													
(*a*) Per cent per degree × 10^2			0.65	−0.12	**2.7 ± 0.6**	**2.8 ± 0.4**	**1.9 ± 0.8**	**3.0 ± 0.6**	**2.4 ± 1.1**	**3.2 ± 0.8**	**0.3 ± 0.2**	**0.8 ± 0.2**	
(*b*) Cc. per gram per deg. × 10^4			0.25	−0.049	**1.3 ± 0.3**	**1.4 ± 0.2**	**0.9 ± 0.4**	**1.4 ± 0.3**	**1.1 ± 0.5**	**1.5 ± 0.4**	**0.15 ± 0.12**	**0.38 ± 0.08**	
Volume increase on inversion $\alpha \longrightarrow \beta$ at t_I													
(*a*) Per cent			2.16		**2.63**		**3.09**		**2.83**		**0.142**		
(*b*) Cc per gram × 10^4			84		**131**		**150**		**132**		**6.3 ± 0.6**		

The inversion temperatures, coefficients of expansion and volume changes on inversion were obtained with a dilatometer holding 60 grams of powder and filled *in vacuo* with a mixture of H_2SO_4 and K_2SO_4 as the expansion liquid. The indices of refraction were measured with a petrographic microscope, using the Becke line method. The values given represent the upper and lower limits, that is, no part of the material showed an index outside of the limits given.

A study of the data given in the table brings out the following facts: (1) The density of raw flint and chalcedony is appreciably lower than, but close to, that of quartz, the difference being not greater than that which might arise from moisture and other impurities in the raw material. The density of the calcined flint is slightly lower but close to that of tridymite. The density of the calcined chalcedony is distinctly lower than that of silica glass, the lightest known form of silica.

(2) The indices of refraction of the raw flint and chalcedony are substantially the same and while close to that of quartz are distinctly lower. The index of the calcined flint is close to that of cristobalite, while the index of the calcined chalcedony is definitely lower than those of cristobalite and tridymite but agrees very well with that of silica glass. As far as these two properties are concerned, therefore, the calcined chalcedony might be considered as a form of silica glass, while the calcined flint might be either cristobalite or tridymite.

(3) Calcined chalcedony shows an inversion point at about 220° and calcined flint one at about 227°. The cristobalite sample studied was prepared from purified flint by a 7 hours calcination at 1500° with sodium tungstate. It showed an inversion temperature of 244° while the sample of tridymite prepared by a similar calcination for 150 hours at 1300° showed an inversion temperature of 117°.

The inversion temperature of cristobalite has been shown by Fenner to depend upon the history of the sample studied and the values obtained for the calcined chalcedony and flint are therefore not inconsistent with the hypothesis that these materials are cristobalite. Such a hypothesis is evidently supported by the values obtained for the volume change on inversion. The results obtained with the dilatometer, therefore, clearly rule out tridymite and if the calcined chalcedony and flint are to be identified with any of the known forms of silica, cristobalite seems to be the only possibility. But if these materials are to be classed as cristobalite it is evident that density measurements or indices of refraction alone or together are insufficient for the identification of the material, since, especially in the case of the calcined chalcedony, both values are very much lower than any of those recorded for cristobalite.

Since the density and index of refraction of the calcined chalcedony seem to indicate that it should be classed as a kind of silica glass, while

the dilatometric data show that it behaves as a kind of cristobalite, some evidence of a more crucial nature seemed necessary before a certain classification of the material could be made. Recourse was therefore had to the determination of the X-ray spectra of the various materials as being the most conclusive evidence that could be secured. Samples of all the materials shown in the table were sent to Dr. A. W. Hull of the General Electric Company who kindly consented to photograph the X-ray spectra. On receipt and comparison of these photographs the following results were obtained. Each spectrum was found to consist of some 25 or more different lines. The spectra of the raw chalcedony, the raw flint, and the quartz were absolutely identical, as were also the spectra of the calcined chalcedony, the calcined flint and the cristobalite This evidence is of such conclusive nature that we are forced to conclude that the calcined flint and chalcedony are composed of cristobalite crystals, while the raw materials are composed of quartz crystals.

How then are we to explain the discrepancy in the density and refractive index data? The following hypothesis seems to be in accord with all of the known facts. Raw chalcedony and flint are colloidal quartz, the individual colloidal crystals being of microscopic or perhaps sub-microscopic size. On calcining the materials the included water is driven out and the individual crystals are transformed *in situ* into cristobalite. The resulting cristobalite crystals would evidently be loosely packed together since in the absence of any flux, there is no opportunity for increase in crystal size. Each cristobalite crystal is thus a colloidal particle made up of a comparatively small number of molecules. The spaces between these colloidal particles of cristobalite must be of sub-microscopic dimensions, so small, in fact, that it is impossible to force a liquid into them. Many of them are possibly completely enclosed. Such a structure would readily account for the very low density displayed by the material. As far as the refractive index is concerned we know that properties such as melting point and vapor pressure depend upon crystal size and it is conceivable that the surface tension forces might also be great enough to distort the crystal form sufficiently to influence the index of refraction. This theory would seem to be borne out by the fact that the calcined chalcedony was not optically homogeneous since different parts of it showed different indices of refraction, the index ranging between 1.456 and 1.470. It is quite possible that many of the crystals are so small that they approach in size the molecules of the liquid phase and the mixture would thus be a colloidal solution of crystals dispersed in their own liquid.

In order to further test the above hypothesis as to the nature of the flint and chalcedony an experiment was made to ascertain whether the density of the calcined chalcedony could be raised by very fine grinding, since if closed pore spaces were present some of these might be disrupted and opened

up by this process. A sample of the material was therefore ground in an agate mortar and the finest particles were separated by stirrring up the material with water and allowing it to settle for 48 hours. The milky supernatant liquid was then removed and evaporated to dryness at low temperature. When sufficient material had been obtained in this way, the average size of the particles was determined with a micrometer microscope and they were found to be 0.0023 mm. in diameter. The density of this material was then measured and found to be 2.224, an increase of 2% over the previous value, this showing definitely the presence of extremely small pore spaces.

The facts, that (*a*) the index of the calcined flint agrees with that of cristobalite and (*b*) its density is much higher than that of the calcined chalcedony are readily explained by the presence of the impurities which are of such a nature as to act as a flux at high temperatures and thus to promote the growth of the cristobalite crystals.

[1] *Amer. J. Sci. New Haven*, **36**, 331(1913). See also Ferguson and Merwin, *Ibid.*, **46**, 417 (1917).

THE FREQUENCY-SENSITIVITY OF NORMAL EARS

BY H. FLETCHER AND R. L. WEGEL

RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY AND WESTERN ELECTRIC COMPANY, INC.

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A large amount of work has been done during the last fifty years in an endeavor to determine in absolute terms the minimum amount of sound that the human ear can perceive. The results obtained by different investigators have varied throughout a very wide range. Two causes contributed to this; namely, that adequate apparatus was not available, and it was not appreciated that so-called normal ears vary so widely in their ability to hear.

The development of the vacuum tube, condenser transmitter, and thermal receiver has given us precision apparatus for work of this kind. In this investigation an air damped receiver was held tightly against the ear by means of a head band. It was actuated by an alternating current which was sent from a vacuum tube oscillator having a range of frequencies from 60 cycles to 6000 cycles per second. By means of a specially constructed attenuator the current entering the receiver could be varied approximately three millionfold. This was accomplished by moving a single dial switch.

By means of condenser transmitters and thermal receivers, this system was calibrated so that from the reading of the attenuator dial switch and the electric current entering it, the alternating pressure impressed upon